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SOLUTION CHEMISTRY IN CREVICES ON Fe-Cr
BINARY ALLOYS

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The major cation concentrations and pH's were measured in crevices on Fe-Cr alloys under potentiostatic conditions in the laboratory and on larger commercial steel specimens freely corroding in natural seawater. Crevice solutions were analyzed by thin-layer chromatography. The effect of increasing Cr in the alloy was to decrease the steady-state pH from pH 4.7 for pure electrolytic iron to a minimum of pH 1.8 for crevice solutions on Fe-25Cr alloy when these materials were potentiostated at +0.300 V vs SCE in 3.5% NaCl solutions. The time required to reach steady-state pH's for the Fe-Cr alloys was also dependent on the Cr content
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of the alloy. In addition, the nature of the crevice corrosion changed from generalized attack for low Cr alloys to localized attack for alloys of 25% Cr or greater. The ratio of the cations in the crevice solutions was not equal to the ratio of the metals in the alloys; the ionic concentrations in the crevice solutions were determined, to a very large extent, by transport phenomena between the crevice and bulk solutions. /

CONTENTS

SOLUTION CHEMISTRY IN CREVICES ON Fe-Cr BINARY ALLOYS

INTRODUCTION

The chemistry of solutions contained within naturally occurring pits, crevices, or stress corrosion cracks has not been well defined. This may largely be attributed to difficulties in obtaining representative samples and in analyzing the small quantities of solution usually available. Thus, it was not uncommon for previous investigators to use large-scale facsimiles of localized corrosion phenomena to obtain solution chemistry data (1-5). Although these macromodels may yield results qualitatively similar to those associated with localized corrosion, it should be appreciated that large-scale laboratory cell experiments may differ kinetically from actual crevices or pits and may accordingly yield solution chemistry data which reflect this difference.

In studies aimed at defining the occluded corrodent in natural localized corrosion forms, representative sampling has continued to be the foremost problem. Among the more notable advances in attempts to improve sampling accuracy was the recently described technique of immobilizing the corrodent within stress corrosion cracks by freezing with liquid nitrogen. The specimen was subsequently broken open mechanically, the corrodent thawed, and the pH and solution composition determined (6,7). Another recent innovation was the use of a capillary to sample the thawed solution from the fracture surface of a stress corrosion crack (8). The sensitivity of colorimetric methods has resulted in their frequent use for the quantitative analysis of the small volumes of solutions from stress corrosion cracks and pits (7,9,10). Electroanalytical methods have also been applied in studies of the local corrodent. Microelectrodes and voltamperometric techniques have been used to measure the pH, dissolved oxygen, and ferrous ion concentrations within active stress corrosion cracks and crevices (11-13).

For the present studies, a capillary technique was adapted to selectively remove micro-volumes of corrodent from crevices on stainless alloys for analysis without prior freezing. Thin-layer chromatographic (TLC) methods were developed for quantitative analysis of the cationic constituents, and narrow range pH indicator papers were used to estimate the acidity. The effects of time and alloy composition on the crevice corrosion of binary Fe-Cr alloys in 3.5% NaCl solution were studied. The results from these accelerated laboratory experiments and long-time seawater immersion studies on commercial stainless steels were compared.

EXPERIMENTAL

Materials

Commercial stainless steel sheets of 405, 409, 410, 430, 434, 446, AM363, ALMAR362, and 304 were cut into 6-in. × 12-in. × 1/2-in. specimens for immersion studies in natural

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seawater. This series of alloys varied in chromium content from 11 to 25% (W/W). For the laboratory studies, 1/8 in. thick sheets of commercial 18Ni maraging steel, 13Cr-8Ni and 304 stainless steels were used to fabricate specimens.

Iron-chromium binary alloys were prepared from high-purity electrolytic metals by vacuum melting and casting. The resulting ingots were forged and hot rolled to 1-in.-diameter rods. The outer 1/16 in. of material then was removed, leaving 7/8-in.-diameter rods. The compositions of the alloys are given in Table 1.

Table 1
Composition of Iron-Chromium Binary Alloys

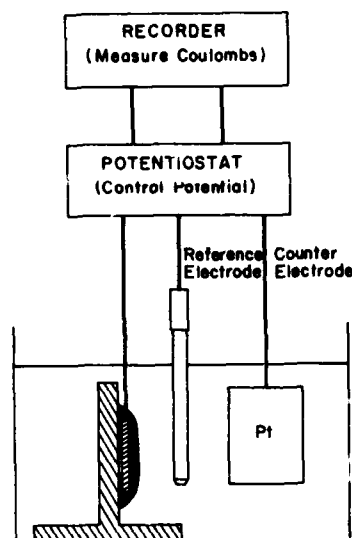| Alloy	% Cr (W/W)
Fe	0.007
Fe-1Cr	0.99
Fe-5Cr	5.0
Fe-10Cr	9.9
Fe-15Cr	14.8
Fe-20Cr	19.5
Fe-25Cr	24.3
Fe-50Cr	48.2
Cr	99.25

The iron-chromium binary alloys were shown to be homogeneous by chemical analysis of samples obtained from different radial and longitudinal portions of the rods. The variation in chromium content among these samples was less than ±0.1% for each of the alloys. Metallographic examination of a cross section from each rod revealed no evidence of microsegregation, a low population of chromic oxide particles, and no appreciable surface oxidation effects. Further confirmation of the microhomogeneity of the alloy was obtained from electron microprobe data (14).

Crevice Assembly Experiments

Disks of 1/16 in. thickness were cut from the 7/8-in.-diameter rods of the binary alloys. The disks were polished on one side through 3/0 papers and rinsed successively with distilled water and 97% ethyl alcohol. Electrical leads were soldered to the unpolished race of each disk. A crevice was formed by arranging a 0.015-in. thickness gauge between each disk and a 2-in. × 2-in. sheet of clear, acrylic plastic. The crevice was fixed in position, and the edges and the external surface of the disk were shielded from the electrolyte by pouring a sealing cement around the disk. When the sealing cement had set, removal of the thickness gauge produced a crevice with the dimensions, 0.9 in. × 0.4 in. × 0.015 in.

Figure 1 shows schematically the major components of the experimental setup during polarization of the crevice. The crevice was mounted vertically in the electrolysis cell, a 1-liter crystallizing dish. A Haber-Luggin capillary containing a saturated calomel reference electrode and a platinum gauze counter electrode ($31.7 \ \mathrm{cm}^2$ in area) completed the cell

2

RECORDER
(Measure Coulombs)

POTENTIOSTAT
(Control Potential)

Reference Counter
Electrode Electrode

Fig. 1 — Schematic diagram of the experimental apparatus

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assembly. No attempt was made to remove dissolved oxygen from the electrolyte. All solutions were prepared with reagent grade chemicals and deionized, double-distilled water. A commercial potentiostat was used to polarize the crevice. The current output leads from the potentiostat were connected to a recorder; integration of the current with respect to time provided an estimate of the total coulombs passed.

In a typical experiment, the crevice was lowered into the electrolyte, 3.5% (W/V) NaCl solution, and trapped air bubbles were removed from the crevice with a small suction bulb. The polarizing current was applied immediately and adjusted to obtain the desired potential. When the experiment was terminated, the crevice was removed from the electrolyte and the exterior surfaces were dried with absorbent tissues. A microcapillary of uniform bore was inserted into the crevice and 1 microliter ($\mu\ell$) of crevice solution was withdrawn. The sample was immediately applied to either pH indicator papers or to sheets of cellulose on an inert matrix for thin-layer chromatography. In some cases the sample was analyzed by conventional colorimetric methods as a check on the results obtained by TLC.

Thin-Layer Chromatography

The elution methods used in conventional paper chromatography and described by Pfeil and his coworkers (15) proved to be suitable for the alloying metals normally found in steel, i.e., iron, chromium, nickel, manganese, and molybdenum. After the sample had been applied to the lower edge of the cellulose sheet end air dried, the sheet was eluted with a solvent consisting of glacial acetic acid, pyridine, and concentrated hydrochloric acid (80:6:20). When the solvent front had advanced to within an inch of the top of the sheet, the chromatogram was removed from the solvent, dried in a horizontal position with a hot air blower, and allowed to stand for 24 hr. The chromatogram was subsequently sprayed with a mixture of concentrated ammonium hydroxide, 30% hydrogen peroxide, and water (1:1:1) to convert the chromic ion to the chromate ion which was readily

3

detected by its yellow color. Spraying the chromatograms with a 1% (W/V) solution of 8-hydroxyquinoline (8-HQ), in ethanol acidified with acetic acid, or a 0.1% (W/V) solution of 1-(2-pyridylazo)-2-napthol (PAN), in ethanol produced highly colored spots of the other cations of interest. The 8-HQ and PAN indicators both produce a yellow background which sometimes obscures the yellow chromate color. In this case a spray of sym-diphenyl carbazide or chromotropic acid will produce pink complexes of chromium which are readily visible. After the chromatogram was dried, the intensities of the spots were enhanced by exposure of the chromatogram to ammonia fumes. The concentrations of the cations in the crevice solutions were estimated by comparison of the size and intensity of the spots with those of standards.

Determination of pH

The use of indicator papers to estimate the pH of the corrodent within stress-corrosion cracks has been questioned because of the possible interferences due to the presence of dissolved salts and the high indicator-to-solution ratio (16). No difficulties from these sources were evident in the present work. Narrow-range commercial pH indicator papers were used, and the sample was applied to a small area of the paper with the aid of a capillary. The reliability of this technique was established by titrating a 10-ml sample of 6N HCl solution which was 0.5M with respect to Fe^{+3}, Mo^{+6}, Mn^{+2}, Ni^{+2}, and Cr^{+3} ions with 1N NaOH solution. The pH of the mixture was measured with a pH meter and with narrow-range pH papers after each increment of NaOH solution was added to alter the acidity of the sample solution. In the pH region tested, from pH 1 to pH 6.5, there was no significant difference in pH values obtained by the indicator papers and the glass electrode.

RESULTS AND DISCUSSION

Thin Layer Chromatograms

A typical chromatogram is shown in Fig. 2. One microliter of solution from a crevice on 18Ni-8Co-3Mo maraging steel which had been exposed to 3.5% NaCl solution at +0.300 V vs SCE for 5 hr was applied at the positions designated by the symbol x. The standard applied at the far right was 0.02M in $FeCl_3$, MoO_3, $MnSO_4$, $NiSO_4$, and $CrCl_3$ dissolved in 6N HCl solution. The limits of detection by the TLC methods used here is 0.0005 mg of iron or chromium in 1 μl of sample. Spots corresponding to Fe, Ni, Co, and Mo ions are discernible on the steel chromatogram. The R_f values of the ions, the ratio of the distance traveled by the ions to that traveled by the solvent, are listed in Table 2. The values obtained in TLC using the methods described above differ from those reported in Ref. 15 for paper chromatography as indicated by comparison of the two sets of data in Table 2.

The areas of the spots were used as an index of approximate concentrations of the cations. Calibration data for the various ions showed that the measured area of the spot of a given cation was a linear function of the logarithm of the cation concentration.
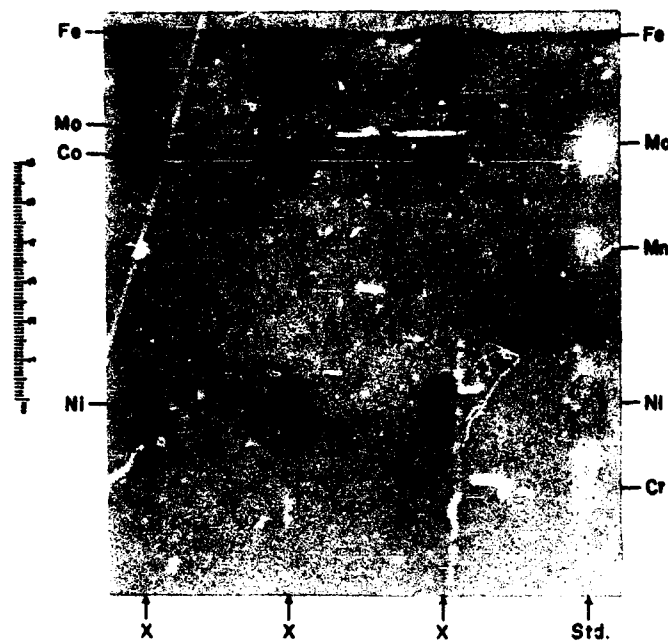
Fig. 2 — Thin layer chromatogram of crevice solution from 18Ni-8Co-3Mo maraging steel in 3.5% NaCl solution for 5 hr at +0.300 V vs SCE

Table 2
R_f Values of Inorganic Ions

Probable Ions	Pfeil, et al. (13)	Observed
Fe^{+2}	0.92	0.99
$MoO_4^=$	—	0.80
Co^{+2}	0.68	0.75
Mn^{+2}	0.57	0.61
Ni^{+2}	0.39	0.34
Cr^{+3}	0.26	0.20

Steady-State in Crevices

The change in crevice pH with time was studied for the Fe-15Cr and Fe-25Cr alloys in 3.5% NaCl solution at a constant potential of +0.300 V vs SCE. Figure 3 shows that for both alloys, the pH of the crevice decreased to a limiting value. Once the limiting value of pH was reached, no further change in pH was observed for times as long as 20 hr. The data in Fig. 3 also indicate that the limiting pH and the time required to attain this value varied with the Cr content of the alloy. The Fe-15Cr alloy attained its limitimg value of pH 3.0 in 1 to 2 hr whereas the Fe-25Cr alloy attained a limited crevice pH of 1.8 after 5 hr. Although not included in Fig. 3, similar data for the Fe-1Cr alloy are consistent with the trends indicated above. The pH of the crevice solution from the Fe-1Cr assembly was 4.6 after 21 hr, and this limiting pH was reached in less than 1 hr.
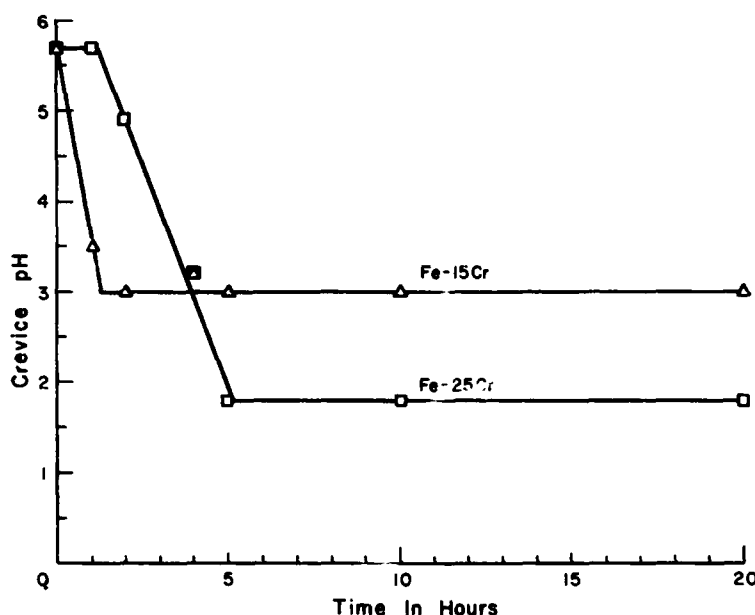

Fig. 3 — Time dependence of crevice pH for Fe-15Cr and Fe-25Cr binary alloys in 3.5% NaCl solution at +0.300 V vs SCE

Analysis for Iron and Chromium in Crevices

Table 3 summarizes the TLC analytical results for ferrous and chromic ion contents of crevices obtained in the series of experiments on Fe-Cr binary alloys. In these experiments the crevices were potentiostated at +0.300 V vs SCE in 3.5% NaCl solution for 5 hr (steady-state attained). The crevice solution in the region of the crevice openings were then sampled and analyzed by the methods described previously. Ferric ions were not detected when samples of the crevice solutions were applied to commercial test papers (minimum sensitivity: 10 ppm Fe^{+3}). Thus, the iron in the crevice solution is concluded

Table 3
Chromium and Iron Contents of Crevice Solutions for Fe-Cr Binary Alloys
Potentiostated at +0.300 √ vs SCE for 5 Hr in 3.5% NaCl Solution

Alloy	Measured mg Fe^{++}	Total mg Fe^{++}	Calculated mg Fe^{++}	Measured mg Cr^{+++}	Total mg Cr^{+++}	Calculated mg Cr^{+++}
Fe-1Cr	0.062	4.6	53	N.D.	N.D.	0.3
Fe-10Cr	0.020	1.5	28	0.003	0.2	1.9
Fe-15Cr	0.012	0.9	20	0.009	0.7	2.2
Fe-20Cr	0.008	0.6	5	0 017	1.3	0.8
Fe-25Cr	0.006	0.5	2	0.068	5.1	0.3

to be predominantly ferrous ions. The measured values in Table 3, columns 2 and 5, are the analytical results for the 1-$\mu\ell$ samples of crevice solution. The total amounts, columns 3 and 6, were obtained by assuming that the crevice solution was of uniform composition throughout and that the 1-μx samples were thus representative of the total crevice volume of 75 $\mu\ell$. The calculated values, columns 4 and 7, were obtained by integrating the current vs time curves to determine the corresponding equivalents of each metal with the assumption that the two metals were anodically discharged in proportion to their occurrence in the alloys.

Consideration of columns 4 and 7, the calculated values of iron and chromium in solution, shows a large decrease in the dissolution of metal with increasing chromium content in the alloy, i.e., a significant decrease in current with increasing Cr content in the alloy.

For each alloy, the total ferrous ion content (column 3) was less than that calculated from the current-time integration (column 4). On the other hand, a disproportionate increase in chromic ion content was measured as the chromium content of the alloy increased (column 6 vs column 7). The disparity between the total and the calculated values for the cation contents in crevices in these experiments can be attributed to two sources: (a) the nonuniformity of the intensity of corrosion within the crevice and (b) the neglect of introducing the effects of transport processes between the crevice and the external solution. The photomicrographs of Fig. 4 clearly show the nonuniformity of the crevice corrosion for the higher Cr alloys. The arrows in the res point to the crevice openings. The Fe-1Cr alloy, which behaves much like pure iron in these experiments, responds to the applied potential uniformly as shown by the etched surface within the crevice. The Fe-10Cr and Fe-25Cr alloys are preferentially attacked at the crevice openings. The central dark regions in the photomicrographs are relatively undisturbed by the applied potential in the 3.5% NaCl solution. The localization of the anodic dissolution in the crevice openings appears to increase with the Cr content of the alloy. Figure 5 shows the results of TLC analysis and pH measurements on 1-$\mu\ell$ samples from the region of the crevice openings and the crevice interior for the Fe-10Cr specimen. The analytical results are clearly consistent with the metallographic observations.
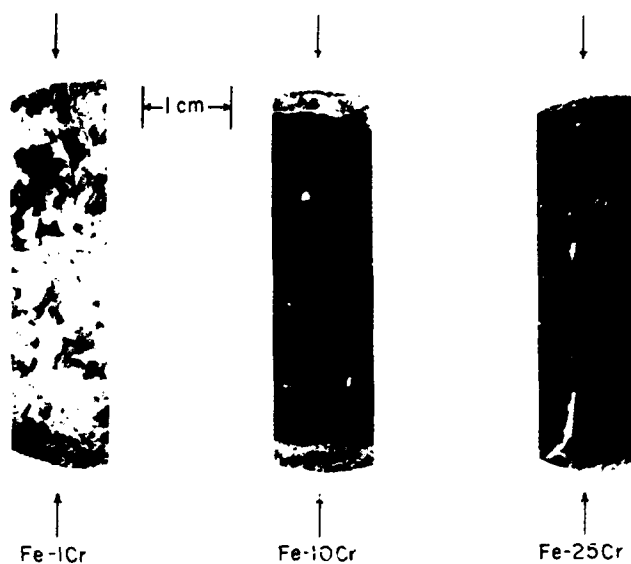
Fe-1Cr   Fe-10Cr   Fe-25Cr

Fig. 4 — Photomicrographs of crevices on Fe-Cr binary alloys after exposure to 3.5% NaCl solution for 5 hr at +0.300 V vs SCE

←— pH=3.2, Fe^{++} = 0.020 mg
Cr^{+++}= 0.003 mg

←— pH=5.0, Fe^{++}= 0.0005 mg
Cr^{+++} Not Detected

←— pH=3.2, Fe^{++}= 0.020 mg
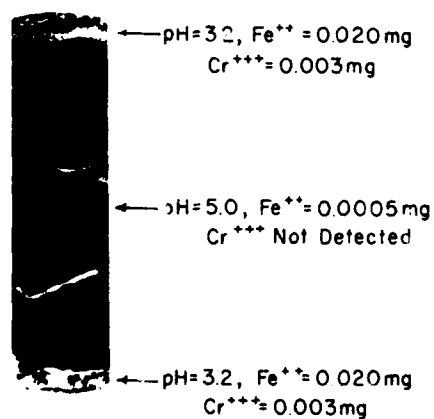Cr^{+++}= 0.003 mg

Fig. 5 — Photomicrograph of a crevice on Fe-10Cr with steady-state concentrations of chromic and ferrous ions, and pH values indicated locally

The preferential anodic dissolution in the vicinity of the crevice openings of Fe-Cr alloys increases the importance of ionic transport processes in influencing the steady-state composition of the occluded corrodent. Ample evidence for substantial transport of ions into the bulk solution was obtained by visual examination and by analysis of the external solution for iron in two selected experiments. The results showed that the major proportion of the iron was in the bulk solution. Clearly, the effects of one or more transport processes — diffusion, migration, and convection of product ions — are of major consequence in determining the solution chemistry in crevices.

Crevice Solution pH

Figure 6 shows the crevice pH (in the vicinity of the crevice opening) plotted against the Cr content of the alloy for Fe-Cr binaries, and three commercial steels when potentiostated at +0.300 V for 5 hr in 3.5% NaCl solution. The data for Fe Cr binary alloys are denoted by the triangle symbols and the commercial steels by the circle symbols. The hatched region delineates the bounds within which crevice pH data were obtained for 10 commercial stainless alloys which were exposed to natural seawater for 12 months at the NRL Key West Marine Corrosion Laboratory. Under the potentiostatic conditions imposed in the laboratory for the Fe-Cr alloys the steady-state crevice pH decreased from 4.7 for electrolytic iron to 1.8 for the Fe-25Cr alloy. For higher Cr contents of the alloy, no further reduction in pH was observed. The pH of crevice solutions from commercial stainless steels after immersion for 12 months in seawater varied between 1.2 and 2.0. The general coincidence between accelerated laboratory experiments and long-time immersion data indicated by Fig. 6 suggests that the former methods may be useful for order of merit predictions on the long term crevice corrosion behavior of this class of alloys.
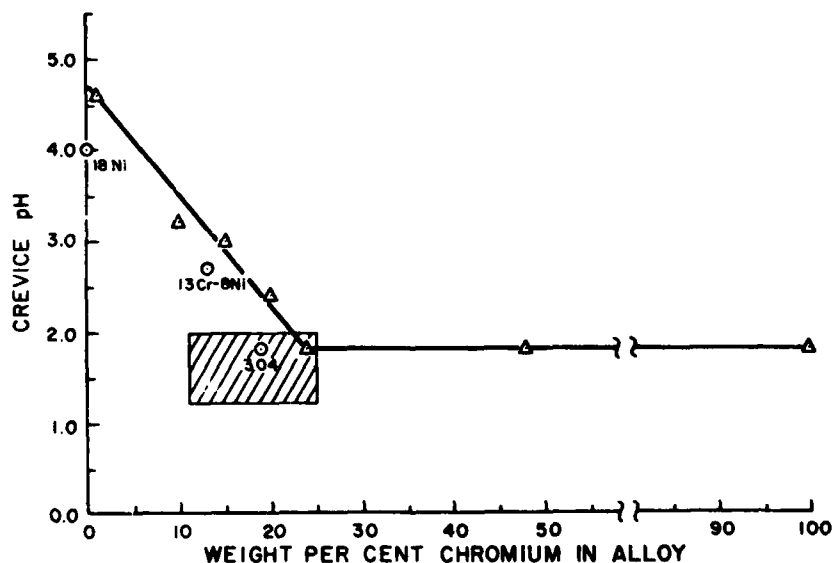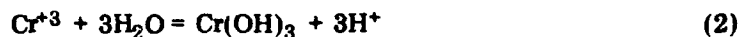

Fig. 6 — Crevice pH of Fe-Cr binary alloys as a function of the chromium content of the alloy

9

The hydrolysis of the anodically generated cations undoubtedly produces the acidity within the crevices. Probable hydrolytic reactions for the ferrous and chromic ions are given by Eqs. (1) and (2).

$$Fe^{+2} + H_2O = FeOH^+ + H^+ \tag{1}$$

$$Cr^{+3} + 3H_2O = Cr(OH)_3 + 3H^+ \tag{2}$$

Use of hydrolysis constants from Hedström (17) and Pourbaix (18), for Fe^{+2} ion and Cr^{+3} ion, respectively, yield the following expressions for the pH for reactions (1) and (2):

$$pH = 4.75 - 1/2 \log [Fe^{+2}] \tag{3}$$

$$pH = 1.60 - 1/3 \log [Cr^{+3}]. \tag{4}$$

The use of expressions (3) and (4) to calculate pH for the crevice solutions by substituting the analytical values for the ferrous and chromic ion concentrations suggest that:

1 The hydrolysis of Fe^{+2} ions dominates and determines the pH of crevice solution for pure iron as well as the Fe-1Cr alloy.

2. The hydrolysis of Cr^{+3} ions determines the pH of crevice solutions for alloys with Cr contents greater that 15%.

3. For intermediate Fe-Cr alloys (less than 15% Cr) the hydrolysis of both cations need to be considered and the use of the simple relations, Eq. (3) or (4) is nullified.

SUMMARY

Crevice corrosion on stainless alloys in these experiments was nonuniform. The metal in the proximity of the crevice opening was preferentially attacked. The area of corrosion increased and advanced into the crevice as the chromium content of the alloy decreased.

A newly developed microsampling technique was capable of selectively removing a microliter of solution from different regions of the crevice. Subsequent TLC analyses and pH measurements of these sample solutions showed compositional differences within the crevice which corresponded to the observed nonuniform corrosion of the specimens.

The relative proportions of iron and chromium, and the total amount of metal in the crevice solutions are not directly proportional to the alloy composition. Rather, the analytical results suggest that ionic transport processes between the crevice and bulk external solution must contribute significantly in determining the composition of the occluded solution.

The measured pH of crevice solutions may be primarily attribu:ed to the hydrolysis of chromic ions for alloys which contain greater than 15% Cr. For alloys containing less than 15% Cr, contributions from the hydrolysis of both cations, Fe^{+2} and Cr^{+3}, appear to be involved in determining the crevice solution pH. The hydrolysis of Fe^{+2} ions appears to dominate and determine the pH of the crevice solution for pure iron and the Fe-1Cr alloy.

The composition of crevice solutions from commercial stainless steel specimens immersed for 12 months in natural seawater were similar to the composition of the crevice solution in potentiostatically accelerated laboratory tests on these commercial alloys in 3.5% NaCl solution.

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REFERENCES

1. H.H. Uhlig, Trans. AIME 140, 411 (1940).

2. E.D. Parsons, H.H. Cudd, and H.L. Lochte, J. Phys. Chem. 45, 1339 (1941).

3. C. Edeleanu and U.R. Evans, Trans. Faraday Soc. 47, 1121 (1951).

4. M.J. Pryor, Corrosion 9, 467 (1953).

5. T. Hagyard and J.R. Santhiapillai, J. Appl. Chem. 9, 323 (1959).

6. B.F. Brown, C.T. Fujii, and E.P. Dahlberg, J. Electrochem. Soc. 116, 218 (1969).

7. G.Sandoz, C.T. Fujii, and B.F. Brown, Corrosion Sci. 10, 839 (1970).

8. H. Leidheiser, Jr. and R. Kissinger, Corrosion 28, 218 (1972).

9. Z.S.-Smialowska, paper presented at the U.R. Evans Conference on Localized Corrosion, Williamsburg, Virginia, Dec. 1971.

10. B.E. Wilde and E. Williams, Electrochimica Acta 16, 1971, (1971).

11. J.A. Smith, M.H. Peterson, and B.F. Brown, Corrosion 26, 539 (1970).

12. G. Butler, H.C.K. Ison, and A.D. Mercer, Brit. Corrosion J. 6, 31 (1971).

13. R.R. Salem, Industrial Lab., U.S.S.R. 26, 206 (1960).

14. C.T. Fujii and R.A. Meussner, NRL Report 5506, Sept. 21, 1960.

15. E. Pfeil, A. Friedrich, and T. Wachsmann, Z. Analyt. Chem. 158, 429 (1957).

16. B.C. Syrett and J.G. Garrison, Tech. Bulletin TB117, Dept. of Energy, Mines, and Resources, Ottawa, 1970.

17. B.O.A. Hedström, Arkiv Kemi 5, 457 (1953).

18. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, New York, 1966. p. 308.